



Electrocatalytic oxidation of formic acid on nano/micro fibers of poly(*p*-anisidine) modified platinum electrode



R.H. Tammam, Mahmoud M. Saleh*

Chemistry Department, Faculty of Science, Cairo University, P.O. 12613, Giza, Egypt

HIGHLIGHTS

- The poly(*p*-anisidine) was synthesized electrochemically.
- The polymer modified Pt used for the first time for FA oxidation in acid medium.
- It shows an enhanced formic acid oxidation.
- The loading level of the polymer is optimized to give maximum rate of the oxidation process.

ARTICLE INFO

Article history:

Received 11 May 2013

Received in revised form

30 June 2013

Accepted 17 July 2013

Available online 25 July 2013

Keywords:

Poly(*p*-anisidine)

Platinum

Formic acid

Fuel cell

Electrocatalysis

ABSTRACT

Poly(*p*-anisidine) (PPA) modified platinum (Pt) electrode shows an extraordinary electrocatalytic activity towards formic acid oxidation in acid medium compared to bare Pt electrode. The Pt/PPA is prepared by electropolymerization of the monomer on Pt electrode in salicylate aqueous solution. The PPA has a fiber-like structure with a thread size of nano- to micrometers. The cyclic voltammogram for formic acid electrooxidation on the Pt/PPA shows no peak for the indirect current and the peak current in the backward sweep is almost equal to that in the forward sweep indicating high electrocatalytic activity for FA oxidation compared to the Pt electrode which shows lower tolerance to CO poisoning. The loading level affects both the onset potential and the peak current of formic acid oxidation. Optimization of the loading level shows that a 5 cycles of polymerization ($11.8 \mu\text{g cm}^{-2}$) is the best loading level of the PPA under the prevailed experimental conditions. The stability of the Pt/PPA towards FA oxidation confirms the higher tolerance to CO poisoning. SEM images and data analysis demonstrate the facilitated oxidation of FA on the Pt/PPA. Interpretation of the enhancement of FA oxidation on the Pt/PPA electrode is introduced.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Fuel cells have been considered for several applications as an important alternative to ordinary energy sources because of its low emission and high power output. Many small organic molecules have shown promising performance as fuels in what is so called direct energy conversion fuel cells. However, some of these small organic molecules show some drawbacks. In direct methanol fuel cell (DMFC), for instance, the methanol concentration cannot exceed some limits (1–2 M), since high rates of fuel crossover reduces the fuel utilization and simultaneously decreases the cell performance [1–3]. Those limitations of methanol caused an increased interest in direct formic acid fuel cells (DFAFCs) [4–6].

Formic acid, on the other hand, is relatively non-toxic and non-explosive compared to MeOH. The DFAFC has an electromotive force (open circuit voltage (OCV)) of ~ 1.48 V which is higher than either hydrogen or direct methanol fuel cells [7]. Platinum and platinum-based catalysts considered to be unavoidable candidate for efficient and durable catalyst for formic acid oxidation [8–13]. However, the platinum surfaces suffer from lower tolerance to CO adsorption and poisoning. Also, high cost of those catalysts is crucial. That is to say, the above failure problems render the commercialization of the DFAFC less practical. Conducting polymers have been used either as coating onto the platinum surface [14,15] or as a dispersion medium for platinum particles [16–20] for enhancing the catalytic activity of Pt surface towards the electrooxidation of formic acid. In this context, the combination of both Pt surface (either as planar or Pt-particles) with a conducting polymer exhibits a synergetic effect and the electrocatalytic activity of the Pt electrodes toward oxidation of small organic molecules

* Corresponding author. Tel.: +20 2 3567 6607; fax: +20 2 3567 7556.
E-mail address: mahmoudsaleh90@yahoo.com (M.M. Saleh).

can be dramatically increased. Such modification by conducting polymers afforded better catalytic effects than Pt for oxidation of organic fuels and offered many advantages such as its easiness and fast preparation by chemical and electrochemical routes.

In the present study and for the first time, poly(*p*-anisidine) modified Pt (Pt/PPA) is used as an anode for electrochemical oxidation of formic acid (FA) from acid solution and the results are compared to that of bare Pt electrode. Cyclic voltammetry, chronoamperometric curves and SEM will be used to demonstrate the electrocatalytic activity of the Pt/PPA towards FA oxidation in acid medium.

2. Experimental

The monomer, *p*-anisidine and all chemicals (purchased from Merck, Sigma Aldrich) were of analytical grade and were used as received without further purification. The working electrodes were polycrystalline Pt ($d = 1.6$ mm) and GC ($d = 3.0$ mm). They were cleaned by mechanical polishing with aqueous slurries of successively finer alumina powder (down to 0.06 μ m) then washed thoroughly with second distilled water. An Hg/Hg₂Cl₂/KCl (sat) (SCE) and a Pt sheet were used as reference and counter electrodes, respectively. Conventional procedure was applied to clean the Pt electrode as described elsewhere [21]. An electrochemical cell with a three-electrode configuration was used in this study. Electrochemical characterizations were performed using system IM6 Zahner elektrik Meßtechnik, Germany.

The electropolymerization process was carried out using 0.01 M *p*-anisidine in 0.1 M sodium salicylate aqueous solution. The polymer film was produced by cyclic voltammetry technique in the potential range from -1.0 – 1.7 V (SCE) for a number of cycles. The polymer then washed with water and dried in air. The catalytic activity of FA oxidation was carried out in an aqueous solution of (0.12 M FA in 0.12 M H₂SO₄). The electrochemical measurements were carried out inside an air thermostat kept at 25 °C (± 0.1 °C). Scanning electron microscope (SEM) images were taken using field emission scanning electron microscope, FE-SEM (FEI, QUANTA FEG 250). The loading level of the polymer film was estimated from the total charge passed through the polymerization process.

3. Results and discussion

3.1. Electrochemical and surface characterizations

Fig. 1A and B show cyclic voltammograms (CV) for the Pt electrode in 0.1 M sodium salicylate solution in the potential range of -1.0 – 1.7 V (SCE) in absence and presence of 0.01 M *p*-anisidine (PA), respectively. In Fig. 1A, the peak “a” denotes the reversible oxidation peak of salicylate ion. The peak “c” corresponds to a dissolution peak of Pt-oxide layers. CV in Fig. 1A in monomer-free solution is similar to that found in literature [22]. In Fig. 1B (in presence of the monomer), the oxidation peak “d” at ~ 0.47 V corresponds to the oxidation of PA and formation of radical cations, which is considered to be the first step in the polymerization of the monomer. The peak at -0.30 V (peak b) is for reduction of the formed polymer. In Fig. 1B and in presence of the monomer, the CV shows similar peaks with those found in literature [23]. The peak height “d” decreases in the consecutive cycles with cycling due to formation of the polymer film which is lower in conductivity than Pt and also due to lower diffusion of the monomer to the Pt surface. The peak “c” increases until the 4th cycle (not shown here) before it decreases to lower currents. In the start, the Pt/PPA enhances the Pt oxides dissolution and then with the increase in cycle number (increase in the thickness), it retards the reduction of the Pt oxides. Note that the peak “a” in Fig. 1A

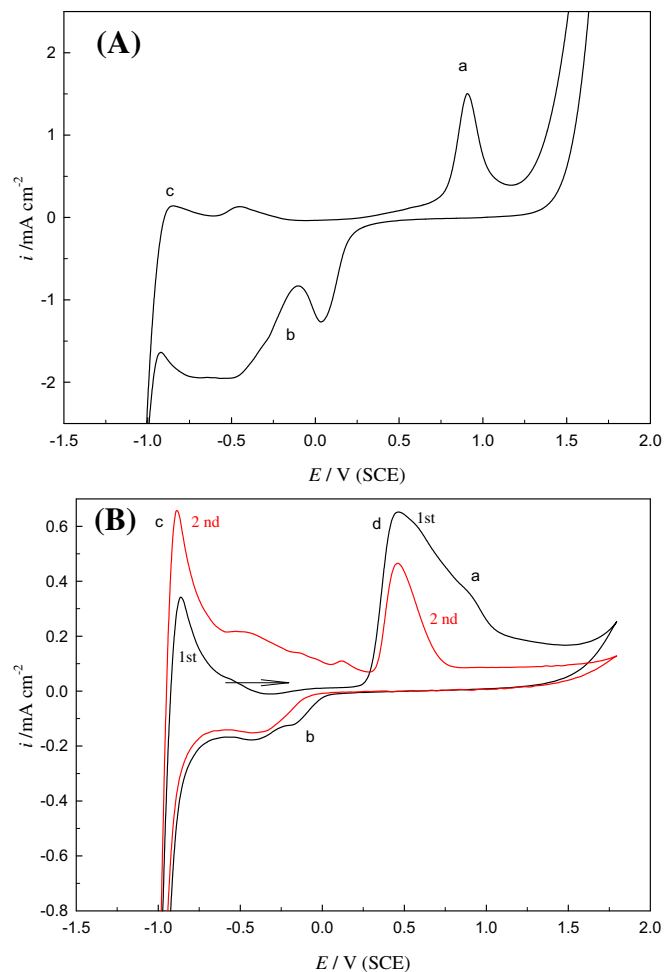


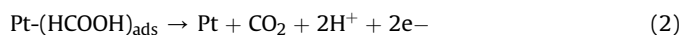
Fig. 1. CVs for Pt electrode in monomer-free 0.1 M sodium salicylate (A) and for electropolymerization of *p*-anisidine from 0.01 M PA + 0.1 M sodium salicylate (B).

converted to a shoulder in Fig. 1B with the potential cycling pointing to the lower currents of the salicylate oxidation on the modified compared to the bare Pt electrode.

The morphology of the formed PPA polymer was examined by taking micro-image using the SEM as shown in Fig. 2. The image was taken for PPA formed after 5 cycles of electropolymerization. The polymer surface is bearing fiber-like structure with a range of thread size from 250 nm to 500 nm (nano- to micro- scale). The small size of the polymer fibers provides high surface area of the polymer with good and uniform distribution of the polymer onto the Pt surface. The Pt surface can be seen as the light areas in the image implying the exposure of the Pt surface to formic acid solution. These features of the Pt/PPA can facilitate the diffusion of liquid fuel to the Pt surface.

3.2. Electrocatalytic oxidation of formic acid

Electrooxidation of formic acid on Pt catalysts follows a well documented dual-pathway mechanism, i.e., direct and indirect oxidation processes involving dehydrogenation and dehydration, respectively [24,25]. In the direct pathway mechanism, i.e., dehydrogenation pathway, HCOOH adsorbed on Pt sites is converted to CO₂ without the formation of poisoning CO_{ads} species:



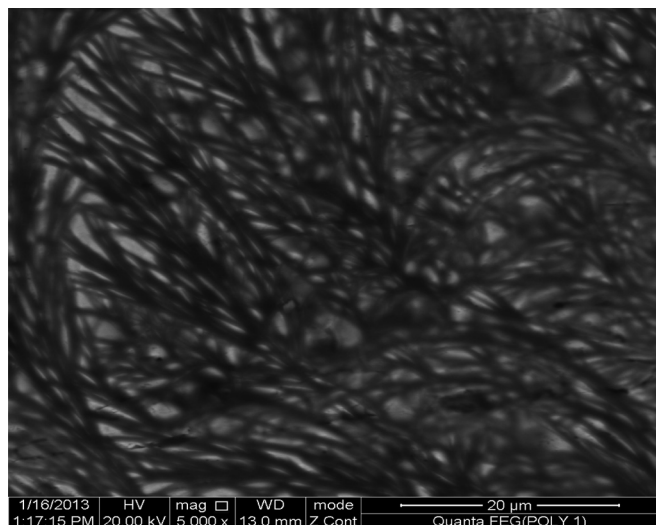
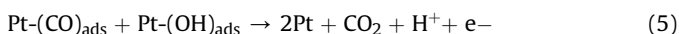
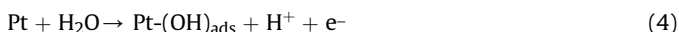


Fig. 2. SEM image of Pt/PPA. Loading level is $11.8 \mu\text{g cm}^{-2}$.

The indirect reaction pathway via dehydration can be written as follows;



The poisonous, CO_{ads} is removed via a reaction involving the OH_{ads} species originated from water dissociation. Cyclic voltammetry studies can be used to decide whether a case of formic acid electrooxidation is dominated by direct or indirect reaction pathway.

Fig. 3 depicts cyclic voltammetric responses for formic acid (FA) oxidation from (0.12 M FA in 0.12 M H_2SO_4) at Pt (A), Pt/PPA (B), Pt_{act} (C) and GC/PPA (D). As seen from Fig. 3 (curve A), Pt shows the usual characteristics of formic acid oxidation on the Pt electrode, which follows the dual-pathway mechanism [5,17,26,27]. The first small

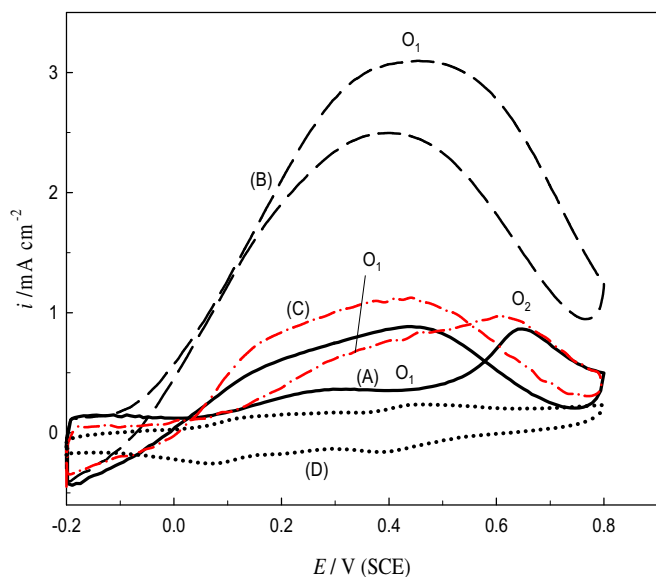


Fig. 3. CVs voltammograms for formic acid oxidation at Pt (A), Pt/PPA (B), Pt_{act} (C) and GC/PPA (D) electrodes from 0.12 M FA + 0.12 M H_2SO_4 using scan rate of 100 mV s^{-1} . PPA loading level is $11.8 \mu\text{g cm}^{-2}$.

peak (O_1) at about 0.25 V is attributed to the direct oxidation of formic acid occurring at the surface sites that remains unblocked by the CO molecules. The second anodic peak (O_2) at approximately 0.65 V is related to the oxidation of the adsorbed CO_{ads} , which results from dehydration of formic acid. The ratio of the two peak current densities ($i_{\text{O}_1}/i_{\text{O}_2}$) is ~ 0.28 , indicating that the electro-oxidation of formic acid on Pt occurs mainly through the dehydration pathway. It can be seen that FA oxidation on Pt electrode shows low current at the peak potential of 0.25 V (O_1) due to lower tolerance towards CO adsorption. At higher positive potential (0.65 V), a second peak is found which corresponds to the indirect oxidation of FA. The backward scan shows a peak current at 0.45 V which is correlated to the FA oxidation on regenerated Pt active sites on the surface. In curve (C), the platinum activated electrode, Pt_{act} was prepared by cycling the potential for 5 cycles in monomer-free solution (i.e., in 0.1 M sodium salicylate) using the same potential range (-1.0 – 1.7 V) which are the same conditions used in the above electropolymerization process. It is well known in literature that cycling the Pt electrode in high potential limits activates the Pt surface towards some electrocatalytic reactions. This was attributed to the dissolution and redeposition of the Pt atoms. The redeposition is accompanied by increase in the Pt surface area [28,29]. In this context, the CV for FA oxidation on Pt_{act} is included here to compare its activity towards FA oxidation with that of the Pt/PPA. This will help to demonstrate whether the catalytic activity of the Pt/PPA is attributed to the activation of the Pt surface (due to potential cycling) or rather, it is attributed to the Pt modification by PPA. Formic oxidation on Pt_{act} (curve C) shows little difference on the peak O_1 and O_2 compared to those on Pt. The peak potential corresponding to peak O_1 doesn't change, whereas, the peak potential corresponding to O_2 is shifted to more negative value which means that the Pt_{act} enhances oxidation of the adsorbed CO. The value of i_{O_1} on Pt_{act} is higher than that at the inactivated Pt electrode. This increase may be attributed to the higher surface area of the Pt_{act} compared to bare Pt. Hence, we can conclude that potential cycling (between -1.0 and 1.7 V) does not have a dramatic effect on Pt activity toward FA oxidation when its results compared with that of the Pt/PPA.

Formic acid oxidation on Pt/PPA (curve B) is bearing different characteristics of its CV compared to bare Pt. At the Pt/PPA two important features were found. The onset potential of the direct FA oxidation, E_{onset} shifts to more negative potential compared to the Pt electrode. For instance, E_{onset} for the FA oxidation is 0.1 and -0.15 at Pt and Pt/PPA, respectively. The peak current of the direct oxidation, i_{O_1} on the Pt/PPA is much higher than that of the Pt electrode indicating the enhancement of FA oxidation on the Pt/PPA electrode. It can be seen that the indirect peak (O_2) is completely disappeared at the Pt/PPA indicating complete tolerance of the modified electrode towards CO poisoning. The value of the peak current, i_{O_1} for direct FA oxidation on the Pt/PPA is 9 folds higher than that on the Pt electrode. These results demonstrate the facilitated FA oxidation on the Pt/PPA compared to the bare Pt. Also, it implies that the Pt/PPA enhances the electrooxidation of FA through the direct pathway. It is clear that Pt/PPA tolerance to the poisoning of the intermediates is much higher than Pt. The CV for FA oxidation on GC/PPA is also shown in Fig. 3 (curve D). The CV reveals no evidence for FA oxidation. One can see that GC/PPA has no electrocatalytic activity towards FA oxidation and yet the presence of both Pt and PPA is necessary for the dramatic increase in the electrocatalytic activity towards FA oxidation on the Pt/PPA.

3.3. Effects of polymer loading

The loading level of the PPA ($\mu\text{g cm}^{-2}$) on the Pt electrode is an important parameter that should be optimized for the

electrocatalytic oxidation of FA on Pt/PPA. It was controlled by the number of cycles during the electropolymerization process. The mass of the polymer (m_{poly}) was determined from the total charge passed during the electropolymerization, Q_{poly} according to the following equation; [30,31]

$$m_{\text{poly}} = \frac{\eta Q_{\text{poly}} M}{FZ} \quad (6)$$

Where m_{poly} is determined assuming a 100% current efficiency, η and M is the molecular weight of *p*-anisidine and F is the Faraday's constant (96485 C mol^{-1}) and Z is the number of electrons transferred per monomer attached to the polymer ($Z = 2$). Using Eq. (6) and the geometric surface area, the loading levels of the polymer in $\mu\text{g cm}^{-2}$ were estimated to be; 7.4, 11.8, 13.8 and $16.1 \mu\text{g cm}^{-2}$ using 2, 5, 7 and 10 cycles respectively.

Formic acid oxidation from (0.12 M FA + 0.12 M H_2SO_4) was performed on the different PPA loading levels as presented in the CVs in Fig. 4. The figure reveals that the peak current, i_{O_1} of the direct FA oxidation increases as the loading level increases from $7.4 \mu\text{g cm}^{-2}$ (curve a) to $11.8 \mu\text{g cm}^{-2}$ (curve b) before it decreases at loading of $13.8 \mu\text{g cm}^{-2}$ (curve c) and $16.1 \mu\text{g cm}^{-2}$ (curve d). The values of E_{onset} are 0.02, -0.15 , -0.09 and -0.05 V for the different loading levels of the polymer, respectively. The order of decrease of the peak current with the loading level is: $11.8 > 13.8 > 16.1 > 7.4 \mu\text{g cm}^{-2}$. It is clear that the best loading level is $11.8 \mu\text{g cm}^{-2}$.

Fig. 5 demonstrates the effects of the loading level on the peak current, i_{O_1} for FA oxidation on the Pt/PPA at different scan rates. The peak current increases as the scan rate increases. At all potential scan rates, the peak current has the same order as shown above ($11.8 > 13.8 > 16.1 > 7.4 \mu\text{g cm}^{-2}$). The results in Figs. 4 and 5 can be discussed as follows. At the low loading level ($7.4 \mu\text{g cm}^{-2}$), the Pt surface is still exposed to the solution and yet the loading of the PPA is not enough to get higher tolerance to CO poisoning. At the higher loading level ($11.8 \mu\text{g cm}^{-2}$), however, the polymer loading (with the nano- and micro- structure (see Fig. 2) offers high surface area of the PPA keeping considerable exposure of the Pt surface (see Fig. 2, the light areas) to the FA solution. Hence, a

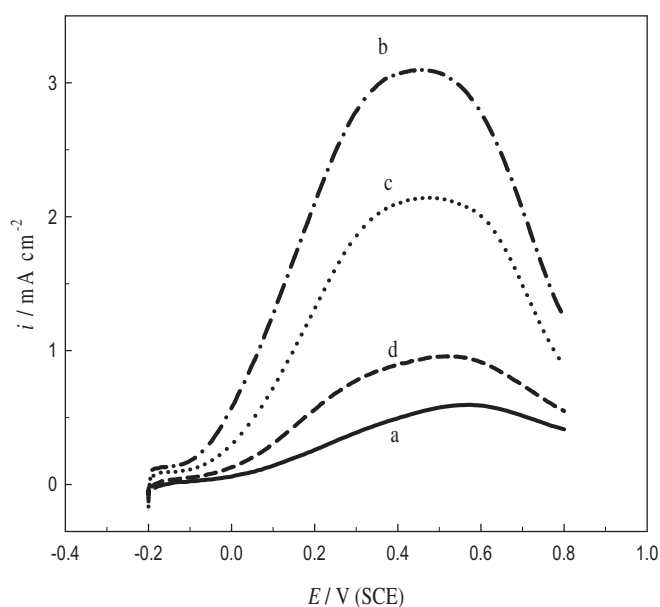


Fig. 4. LSV for oxidation of formic acid at Pt/PPA electrode from 0.12 M FA + 0.12 M H_2SO_4 using scan rate of 100 mV s^{-1} at different PPA loading levels, a) 7.4, b) 11.8, c) 13.8 and d) $16.1 \mu\text{g cm}^{-2}$.

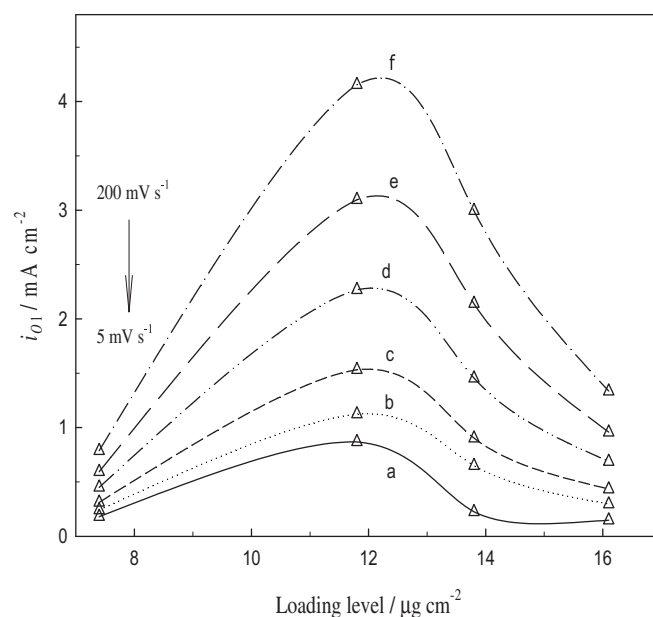


Fig. 5. The peak current density of FA oxidation on Pt/PPA in 0.12 M FA + 0.12 M H_2SO_4 at different PPA loading levels and at different scan rates: a) 5, b) 10 c) 20 d) 50 e) 100 and f) 200 mV s^{-1} .

synergistic effect between the Pt and the PPA is achieved. The last consideration may interpret the higher enhancement obtained with a loading level of $11.8 \mu\text{g cm}^{-2}$ compared to the other loadings. At loading levels higher than $11.8 \mu\text{g cm}^{-2}$, the thicker polymer films render the diffusion of FA to the Pt surface more difficult which make the diffusion a predominant factor. The onset potential at any scan rate follows the same above order. We can say, lower currents were obtained at loading levels of 13.8 and $16.1 \mu\text{g cm}^{-2}$. The above trend can be explained under the following considerations. There is a trade-off between the synergism between PPA and Pt substrate and the decrease in the rate of diffusion of the FA as the loading of the polymer increases. Another consideration is the increase in the polymer resistance with the loading levels higher than $11.8 \mu\text{g cm}^{-2}$.

Fig. 6 depicts a plot of the peak current, i_{O_1} with the square root of the potential scan rate ($v^{0.5}$) for FA oxidation on the Pt/PPA with loading level of $11.8 \mu\text{g cm}^{-2}$ of the polymer. The relation gives a straight line ($R^2 = 0.998$) which suggests that the oxidation of formic acid on the Pt/PPA is a diffusion controlled process [32,33].

For further evaluation of the electrocatalytic activity and stability of the Pt/PPA anode, chronoamperometric measurements were conducted during the electrooxidation of FA at the Pt and Pt/PPA electrodes in 0.12 M FA and 0.12 M H_2SO_4 at 0.4 V. Chronoamperometric curves are shown in Fig. 7. As revealed from the figure the current decreases with time at both electrodes which is attributed to the intermediate poisoning species formed during FA electrooxidation. It can be recognized that Pt/PPA gives higher currents than bare Pt demonstrating that Pt/PPA has better poisoning tolerance ability than bare Pt. The current in the case of Pt/PPA electrode decreases after much longer time than of the Pt electrode which indicates much better electrocatalytic stability than bare Pt.

3.4. Mechanism of FA oxidation on the Pt/PPA

So far, the results presented here showed enhanced electrocatalytic activity towards the electrooxidation of FA on PPA modified Pt electrode. As discussed above, the FA oxidation at Pt

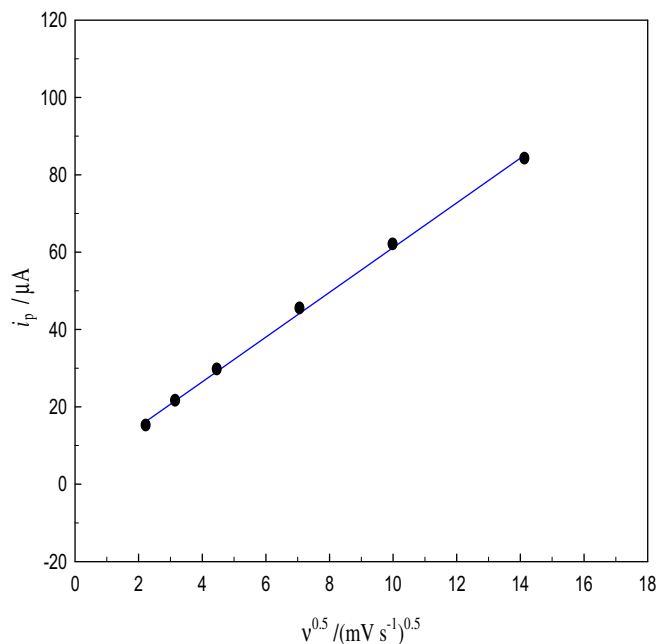


Fig. 6. The plot of the peak current of FA oxidation at Pt/PPA vs the square root of the scan rate. The solution is 0.12 M FA + 0.12 M H₂SO₄ and loading level is 11.8 μg cm⁻².

electrode proceeds via either the direct or indirect oxidation pathways. The indirect pathway involves the oxidation of the poisonous, CO resulting from the “non-faradaic” dehydration of formic acid. The generation of CO molecules hinders the availability of the Pt active sites and thus prevents the surface hydroxylation (OH_{ad}), which is believed to be a main step for favoring the direct oxidation path. The redox conducting polymer such as PPA participates in the reaction mechanism by facilitating charge transfer of the possible steps during FA oxidation. Fig. 3 (curve D) demonstrates that the PPA alone (electropolymerized on GC, i.e., GC/PPA) cannot initiate FA oxidation and hence Pt exposed areas together with the PPA fibers are essential components for the dramatic increase in the rate of FA oxidation.

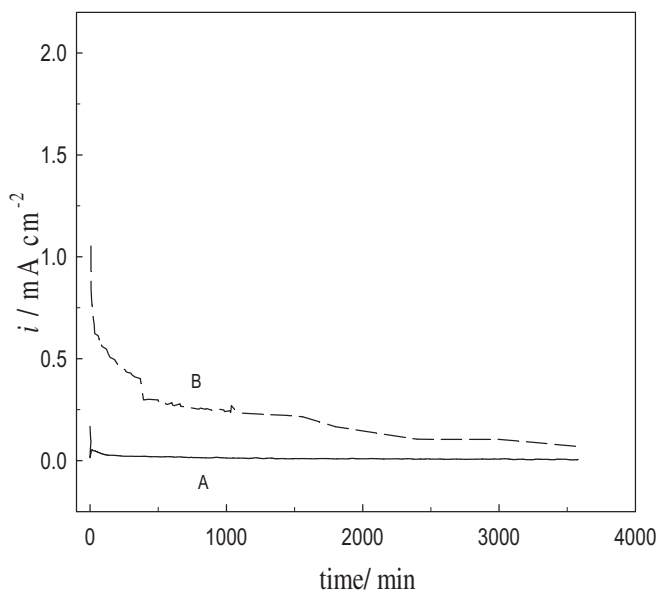


Fig. 7. Chronoamperometric curves of FA oxidation at 0.4 V (SCE) at A) Pt and B) Pt/PPA electrode from 0.12 M FA + 0.12 M H₂SO₄. PPA loading is 11.8 μg cm⁻².

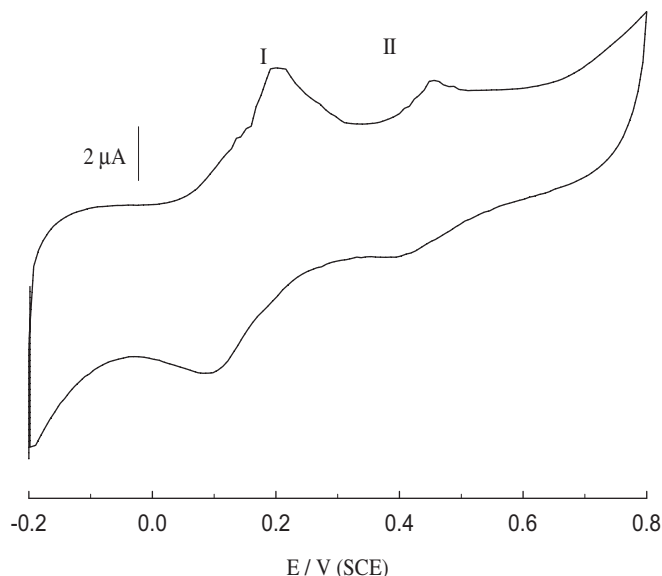


Fig. 8. CV of Pt/PPA in 0.1 M H₂SO₄ with scan rate of 100 mV s⁻¹. Loading level of PPA is 11.8 μg cm⁻².

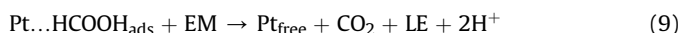
Two possibilities can discuss the origin of enhancement of FA oxidation on the Pt/PPA. First: the PPA facilitates the oxidation of the adsorbed CO molecules at a reasonably low potential. The second: the redox polymer (PPA) may act as a catalytic mediator through a reversible transformation between the different redox forms of the PPA that can facilitates the charge transfer during the direct oxidation of FA to CO₂.

An attempt is suggested here for plausible mechanism via some equations to demonstrate the explanation of the observed enhancement of FA oxidation on the Pt/PPA. The PPA exists in different redox forms and when the applied potential varies from -0.2 to +1.0 V, PPA changes its form and exhibits different chemical and physical properties. The only electrically conducting form is an emeraldine salt (EM), which is the protonated form of the emeraldine base. The protonated emeraldine (EM) form is produced by the oxidation of leucoemeraldine (LE) in aqueous acids [34]. These processes of redox transitions are clearly shown in Fig. 8. The features in the CV for Pt/PPA (loading level of 11.8 μg cm⁻²) which was recorded in FA-free solution 0.12 M H₂SO₄ solution is similar to those found in literature [35,36].

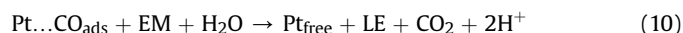
The 2nd possibility introduced above can be discussed in the light of the following discussion. According to E. Laviron [37], who studied the electron transfer mediated by redox polymer electrodes, when the redox potential of the system in solution (FA in our case), $E_{O,2}$ is more positive than the redox potential of the redox polymer, $E_{O,1}$ (PPA in our case), the transfer of electron is always possible. According to the above author also, when $E_{O,2} < E_{O,1}$, on the contrary, the transfer is possible only if $(E_{O,1} - E_{O,2})$ is smaller than 0.3 V. In our case and according to Figs. 3 and 8, the difference $(E_{O,1} - E_{O,2})$ is about 0.1 V and hence charge transfer is possible. The polymer, PPA is known (as many of the polyaniline derivatives) of their redox property with a reversible transformation between the reduced form (LE) and the oxidized form (EM);



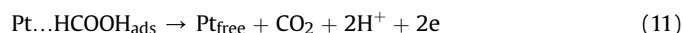
Eq. (8) can be assigned to peak I appears in Fig. 8 which is for oxidation of LE to EM at peak potential of 0.2 V. The oxidized polymer, EM which is generated, reacts with FA as seen below;



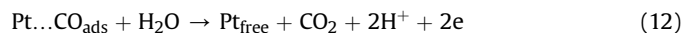
and/or



Addition of Eqs. (8)–(9) gives:



Also, addition of Eqs. (8) and (10) gives:



Eqs. (11) and (12) demonstrate that the observed oxidation current is solely supported by the oxidation of FA, and the conducting polymer functions as a catalytic mediator. Moreover, Reactions (9) and (10) indicate the regeneration of LE which is believed to start new cycles of catalytic mediation through the above set of equations. In principle, EM species can regenerate the Pt active sites for the further oxidation to proceed.

4. Conclusions

Poly(*p*-anisidine) (PPA) electropolymerized on Pt electrode showed a fiber-like structure and revealed an enhanced formic acid (FA) oxidation in H₂SO₄ solution. The polymer fiber had a nano- to micro-size of 250–500 nm and its loading has been controlled by controlling the number potential cycles during the electropolymerization process. The Pt/PPA shifted the onset potential of FA oxidation to more negative value and increased the peak current up to more than 9 folds higher than that of the unmodified bare Pt. The loading level affects both the onset potential and the peak current and optimization of the loading level showed that a 5 cycles or 11.8 μg cm^{−2} is the best loading level under the prevailed experimental conditions. Lower loading levels than 11.8 μg cm^{−2} do not afford tolerance to CO poisoning and loading levels higher than 11.8 μg cm^{−2} cause slower diffusion of the FA to the Pt surface. A plausible mechanism for FA oxidation on Pt/PPA and discussion of the enhancement of the FA on the modified electrode was presented.

References

- [1] C. Rice, S. Ha, R.I. Masel, P. Waszczuk, A. Wieckowski, T. Barnard, J. Power Sources 111 (2002) 83.
- [2] Y.W. Rhee, S.Y. Ha, R.I. Masel, J. Power Sources 117 (2003) 35.
- [3] A. Capon, R. Parsons, J. Electroanal. Chem. 45 (1973) 205.
- [4] T. Iwasita, Electrochim. Acta 47 (2002) 3663.
- [5] X. Wang, J.M. Hu, I.M. Hsing, J. Electroanal. Chem. 562 (2004) 73.
- [6] C. Rice, S. Ha, R.I. Masel, A. Wieckowski, J. Power Sources 115 (2003) 229.
- [7] X. Yu, P.G. Pickup, J. Power Sources 182 (2008) 124.
- [8] Z.H. Zhang, X.C. Zhou, C.P. Liu, W. Xing, Electrochem. Commun. 10 (2008) 131.
- [9] S. Zhang, Y. Shao, G. Yin, Y. Lin, J. Power Sources 195 (2010) 1103.
- [10] K. Kaneto, J. Nakajima, M. Nakagawa, W. Takashima, Thin Solid Films 438 (2003) 195.
- [11] A. Ramanavicius, A. Ramanaviciene, A. Malinauskas, Electrochim. Acta 51 (2006) 6025.
- [12] T.A. Rajesh, D. Kumar, Sens. Actuators B Chem. 136 (2009) 275.
- [13] M.J. Croissant, T. Napporn, J.-M. Léger, C. Lamy, Electrochim. Acta 43 (1998) 2447.
- [14] M. Choy, F. Hahn, J.-M. Léger, C. Lamy, J.M. Ortega, Thin Solid Films 515 (2007) 3611.
- [15] L. Meichao, W. Wuyang, M.A. Chun'an, Chin. J. Catal. 30 (11) (2009) 1073.
- [16] V. Selvaraj, M. Alagar, I. Hamerton, Appl. Catal. B Environ. 73 (2007) 172.
- [17] V. Selvaraj, M. Alagar, K.S. Kumar, Appl. Catal. B Environ. 75 (2007) 129.
- [18] P. Ocón, P. Herrasti, S. Rojas, Polymer 42 (2001) 2439.
- [19] K.S. Ryu, N.G. Park, K.M. Kim, Y.G. Lee, Y.J. Park, S.J. Lee, C.K. Jeong, J. Joo, S.H. Chang, Synth. Met. 135–136 (2003) 397.
- [20] I. Becerik, F. Kadirgan, Turk. J. Chem. 25 (2001) 373.
- [21] M.I. Awad, M.M. Saleh, T. Ohsaka, J. Power Sources 196 (2011) 3722.
- [22] S. Chaudhari, A.B. Gaikwad, P.P. Patil, Curr. Appl. Phys. 9 (2009) 206.
- [23] A.T. Ozyilma, G. Ozyilma, O. Yigitoglu, Prog. Org. Coatings 67 (2010) 28.
- [24] W. Zhou, J. Xu, Y. Dub, P. Yang, Int. J. Hydrogen Energy 36 (2011) 1903.
- [25] G.Q. Lu, A. Crown, A. Wieckowski, J. Phys. Chem. B 103 (1999) 9700.
- [26] R.S. Jayashree, J.S. Spendelow, J. Yeom, C. Rastogi, M.A. Shannon, P.J.A. Kenis, Electrochim. Acta 50 (2005) 4674.
- [27] V. Selvaraj, A.N. Grace, M. Alagar, J. Colloid Interf. Sci. 333 (2009) 254.
- [28] X. Wei, A. Reiner, E. Müller, A. Wokaun, G.G. Scherer, L. Zhang, K.-Y. Shou, B.J. Nelson, Electrochim. Acta 53 (2008) 4051.
- [29] G. Tremiliosi-Filho, G. Jerkiewicz, B.E. Conway, Langmuir 8 (1992) 658.
- [30] J.K. Xu, G.M. Nie, S.S. Zhang, X.J. Han, J. Hou, S.Z. Pu, J. Polym. Sci. A Polym. Chem. 43 (2005) 1444.
- [31] W.Q. Zhou, C.Y. Zhai, Y.K. Du, J.K. Xu, P. Yang, Int. J. Hydrogen Energy 34 (2009) 9316.
- [32] W. Zhou, Y. Du, H. Zhanga, J. Xu, P. Yang, Electrochim. Acta 55 (2010) 2911.
- [33] Y.C. Zhao, X.L. Yang, J.N. Tian, F.Y. Wang, L. Zhan, Int. J. Hydrogen Energy 35 (2010) 3249.
- [34] G. Inzelt, Conducting Polymers: a New Era in Electrochemistry, in: F. Scholz (Ed.), Monographs in Electrochemistry, Springer-Verlag, Berlin Heidelberg, 2008.
- [35] T.F. Otero, I. Boyano, J. Phys. Chem. B 107 (2003) 4269.
- [36] Xin-Gui Li, W. Duan, Mei-R. Huang, L.N.J. Rodriguez, Reactive Funct. Polym. 62 (2005) 261.
- [37] E. Laviron, J. Electroanal. Chem. 131 (1982) 61.